Notes on the calculation of Transition Density Matrices (TDM)

In the molecular orbital (MO) basis, the TDM between excited states I and J can be writen as:

$$\rho^{IJ}_{MO_{pq}} = \langle \Psi_I | a_p^\dagger a_q | \Psi_J \rangle, \qquad (1)$$

where $a_p^\dagger$ and a_q are creation and annihilation operators acting on the virtual MO p and the occupied MO q, and the excitation states wavefunctions are given by:

$$|\Psi_J\rangle = \sum_{ia} X_{ia}^{(J)} |\Phi_i^a\rangle, \qquad (2)$$

where $|\Phi_i^a\rangle$ is a single Slater determinant representing the transition from the occupied MO i to the virtual orbital a, which can be cast in terms of the ground state (GS) solution $|\Phi_0\rangle$ (also given by a single Slater determinant) as:

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle, \qquad (3)$$

and $X_{ia}^{(J)}$ are the corresponding configuration interaction singles (CIS) coefficients for excited state J. Analogously we have:

$$|\Psi_I\rangle = \sum_{jb} X_{jb}^{(I)} |\Phi_j^b\rangle, \qquad (4)$$

and:

$$|\Phi_j^b\rangle = a_b^\dagger a_j |\Phi_0\rangle$$

Combining eqs. 1-5 we get:

$$\langle \Psi_I | a_p^\dagger a_q | \Psi_J \rangle = \sum_{ia}\sum_{jb} (X_{jb}^{(I)})^* \langle \Phi_0 | a_j^\dagger a_b a_p^\dagger a_q a_a^\dagger a_i | \Phi_0 \rangle X_{ia}^{(J)}, \qquad (6)$$

The string of creation and annihilation operators can be calculated by means of the Wick's theorem, which allows to write it as a summation of the possible three pairs of concatenated creator and annihilator operators. Contractions including $a_j^\dagger a_b$, $a_p^\dagger a_q$, or $a_a^\dagger a_i$ render transitions to the same MO which have zero weight in the excited state expansion. The only non-trivial contributions are:

$$a_j^{\dagger} a_b a_p^{\dagger} a_q a_a^{\dagger} a_i \rightarrow (-1)^3 \delta_{jq} \delta_{ab} \delta_{ip}, \tag{7}$$

and:

$$a_j^{\dagger} a_b a_p^{\dagger} a_q a_a^{\dagger} a_i \rightarrow (-1)^4 \delta_{ij} \delta_{bq} \delta_{qa}, \tag{8}$$

From eq. 7 we get for the occupied block of the TDM:

$$\rho^{IJ}_{MO_{ij}} = -\sum_a (X^{(I)}_{ja})^* X^{(J)}_{ia}, \tag{9}$$

From eq. 8 we get for the virtual block of the TDM:

$$\rho^{IJ}_{MO_{ba}} = \sum_i (X^{(I)}_{ib})^* X^{(J)}_{ia}, \tag{10}$$

Taking into account that the TDM for transitions from the GS to any given state can be cast as:

$$\rho^{(0J)}_{MO_{ia}} = \begin{pmatrix} 0_{oo} & X^{(J)}_{ov} \\ 0_{vo} & 0_{vv} \end{pmatrix}, \tag{11}$$

where the blocks 0_{oo}, 0_{vo}, and 0_{vv} are empty block representing occupied-occupied, virtual-occupied, and virtual-virtual contributions, respectively. Then we can write eqs. 9-10 in a simplified matrix notation:

$$\rho^{IJ}_{MO} = \left((\rho^{0I}_{MO})^T \rho^{0J}_{MO} - \rho^{0I}_{MO} (\rho^{0J}_{MO})^T \right), \tag{12}$$

which takes the same form in the atomic orbital (AO) basis:

$$\rho^{IJ}_{AO} = \left((\rho^{0I}_{AO})^T \rho^{0J}_{AO} - \rho^{0I}_{AO} (\rho^{0J}_{AO})^T \right), \tag{13}$$